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The use of isotopes for improved management of nitrate pollution in aqueous resources

Edited by S. Duta, F. Accoe, P. Taylor

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Contact information
Address: Retieseweg 111, B-2440 Geel, Belgium
E-mail: philip.taylor@ec.europa.eu
Tel.: + 32 (0) 14 571 605
Fax: + 32 (0) 14 571 863

http://irmm.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

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Abstract

The objective of this paper is to create awareness with environmental managers for the potential offered by the use of isotope data when tackling the environmental management of nitrate contamination in ground and surface water.
The paper shows how such data can lead to source apportionment or detection of natural attenuation of nitrate pollution in surface and groundwater, how it is complementary to existing water quality monitoring data and how it enables those involved in the implementation of environmental policy to develop more effective remedial measures and management strategies.
The paper describes when and how to set up such studies, what can be expected as outcome and describes the benefits and limitations.
The above topics will be demonstrated via a number of case studies conducted in Europe where isotope data lead to a better understanding of the origin, degree of natural attenuation or transport processes of nitrate pollution in surface or groundwater.

1. Introduction

Nitrate pollution is still a major concern in many European aqueous resources, which may originate from multiple sources: excess application of mineral nitrogen (N) fertilizers and animal manure in agriculture, discharges from urban or industrial N bearing waste water, septic leachate in unsewered areas, atmospheric deposition or decomposition of soil organic N. In addition to the existence of multiple potential nitrate sources, nitrate pollution may originate from present as well as from historical land use, which complicates the problem.
In the framework of the Nitrates Directive (91/976/EEC) and the Urban Wastewater Directive (91/271/EEC), several policy measures with major socio-economic impact have been implemented to reduce nitrate inputs from agriculture or urban and industrial waste water. The Water Framework Directive (2000/60/EC) and Nitrates Directive require that the chemical water quality (concentration of nitrate and other ions) is monitored by the national environment agencies (currently in about 22.000 surface water and 20.000 groundwater sampling stations in the EU15) to evaluate the effectiveness of the measures taken. Despite all the efforts made so far, increasing nitrate concentrations were still observed in a significant amount of groundwater and surface water monitoring sites (36% and 14%, respectively) during the monitoring period 2000-2003.
The development and implementation of effective remediation measures in nitrate polluted areas requires identification of the actual pollution sources, which can not be achieved based on the current water quality monitoring data alone (concentration measurements). The objective of this paper is to create awareness with environmental managers for the potential offered by the use of isotope data when tackling the environmental management of nitrate contamination in ground and surface water. We want to demonstrate how such data can lead to source apportionment of nitrate pollution (= identification of the sources and estimation of their contribution) in surface and groundwater, how it is complementary to existing water quality monitoring data and how it enables those involved in the implementation of environmental policy to develop more effective remedial measures.
The above topics will be demonstrated via a number of case studies conducted in Europe where isotope data lead to a better understanding of the origin, degree of natural attenuation or transport processes of nitrate pollution in surface or groundwater.

2. How isotopes can be used for nitrate source apportionment

Nitrates originating from different pollution sources generally have a distinctive nitrogen (N) or oxygen (O) isotopic signature (ratio of the heavy to light stable isotope) (Fig. 1). Therefore, stable isotope analysis of nitrate in water can be used to identify the nitrate sources and to estimate their contribution to nitrate pollution. In addition, biological cycling of N often affects the isotopic composition in a predictable pattern, which can be used to detect and quantify natural nitrate removal processes (denitrification) (Kendall, 1998).

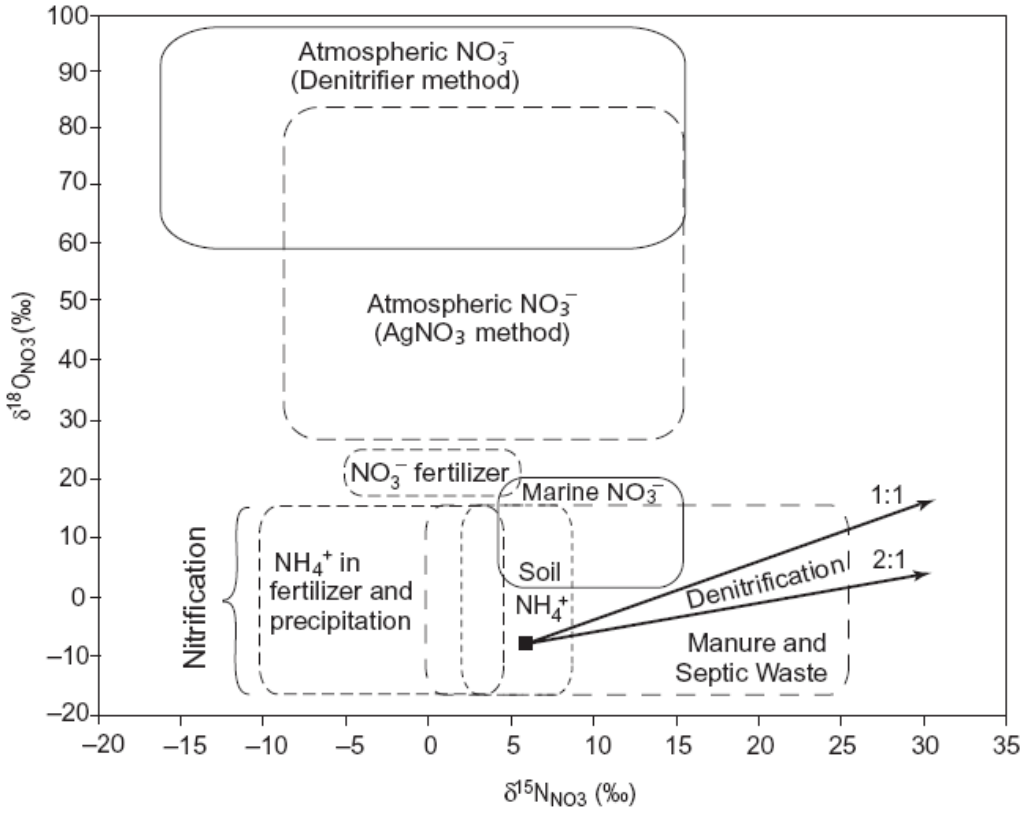

Fig. 1. Typical values of N and O isotope ratios (expressed in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values) of nitrate derived from various N sources (taken from Kendall et al, 2007)

The isotopic signature of tracers that migrate along with nitrate (e.g. boron, strontium, sulphate S and/or O) can often give additional information on the sources of pollution (e.g. Widory et al., 2004; Vitoria et al., 2008).
Finally, stable and radio-active isotopic signatures of water (deuterium, tritium, oxygen) can give valuable insight into timescales and transport behaviour of nitrate pollution in groundwater (e.g. Bohlke and Denver, 1995; Kendall and Caldwell, 1998; Wassenaar et al, 2006).

3. How isotope data are complementary to existing water quality monitoring data

Monitoring nitrate concentrations and other water quality parameters enables to identify nitrate problem regions where remedial actions are needed and to follow up nitrate pollution trends.
In areas where the major nitrate pollution sources are well known, the effectiveness of remedial actions taken to reduce nitrate input from these sources can be evaluated by monitoring nitrate concentration trends. However, when multiple potential nitrate sources exist, identification of the main sources and estimation of their contribution is essential for environmental policy makers to implement effective, source-oriented remediation measures. This information can not be deducted from the current water quality monitoring data alone (concentration measurements). In addition, interpretation of the relation

between nitrate concentration data in surface or groundwater monitoring points and nitrate input from the sources is complicated by time delaying mechanisms (percolation through soil, groundwater flow) and biogeochemical processes altering the concentration during nitrate transport.
Isotope data can thus be used as a powerful tool, complementary to existing monitoring data, since they enable to identify the nitrate sources, to asses their relative contribution to nitrate pollution and to quantify nitrate transport and removal processes.

4. How to set isotope studies, expected outcome, expertise needed

Sampling, chemical and isotope analysis

Selection of the water sampling locations and timing can be based on available water quality monitoring data from the local environment agency. The sampling strategy (number of samples, time of sampling, sampling frequency) is very dependent from case to case (size of the study area, ground or surface water study). Water samples for chemical analysis of major ion concentrations (nitrate, chloride, sulphate etc.) and stable isotope analysis can be collected in a similar way according to procedures described by Clark and Fritz (1997). Specific guidelines for sampling and sample amounts needed are generally supplied by the stable isotope analysis laboratory. When the potential nitrate sources are identified, samples from these sources are also needed for chemical and isotopic characterization.
Validated methods, instrumentation and expertise for the analysis of various stable isotopes (nitrate N and O, boron, strontium, sulphate S and O, deuterium, tritium, oxygen in water) are available in several laboratories across Europe.

Interpretation of the isotope data

Isotope data are most successfully interpreted in combination with the conventional geochemical water quality data and hydrogeological data of the study area.
The geochemical water quality parameters (concentrations of nitrate and other major ions like chloride and sulphate) are generally monitored by and available from the local environmental agencies. Concentration data of the isotope tracers considered in the study (nitrate, boron, strontium) are also essential for interpretation of the respective isotope data. Knowledge on the hydrogeology and geographical setting of the study area is necessary in order to understand the main water flow and nitrate transport directions. The geochemical transformations which may potentially occur during transport of the nitrate or co-migrating tracers should also be well understood, since these transformations may affect both concentration and isotopic signature of the tracers. Data concerning hydrogeology, geography and geochemistry of the study area can usually be obtained from the national geological survey. Different approaches can be used for interpretation of the data, which may result in qualitative estimation or quantitative determination of source contributions. Interpretation of bivariate plots (isotope ratio versus the concentration of a tracer) can be used to study mixing processes of nitrate sources. Interpretation of the multiple isotope and chemical tracer data for source apportionment usually requires advanced multivariate statistical analysis techniques (like discriminant analysis, principal components analysis) or classification trees (e.g. Spruill et al., 2002). The contribution of different nitrate sources to a mixture can be quantified using isotope mixing models based on mass balance equantions (e.g. Philips and Gregg, 2001; Deutsch et al, 2006).

Expertise needed for conducting isotope studies and data interpretation

For successfully conducting isotope studies and interpretation of the data, multi-disciplinary expertise is thus needed in the following areas:

- stable isotope analysis
- hydrogeology and geochemistry
- isotope geochemistry (interaction between biological or chemical processes and isotopic composition of the tracers)
- advanced statistical data analysis

5. The Isotopes for improved management of Nitrate Pollution in Aqueous Resources (INPAR)

Many research activities are going on in different institutes across Europe using isotope techniques for management of nitrate pollution in water. In 2006, the INPAR network (Isotopes for improved management of Nitrate Pollution in Aqueous Resources) has been set up by JRC-IRMM to bring together this international expertise and to stimulate the exchange of the multi-disciplinary know-how (stable isotope analysis, hydrogeology, (isotope) geochemistry, advanced statistical data analysis).
The main aims of the network are to:

- share scientific and technical knowledge (both theoretical and practical) regarding isotopic measurements for the better management of water resources with a special focus on nitrate
- set up joint research projects in this domain, funded from European or national funding
- exchange staff as the methodology becomes more common in the water management domain
- explore, define and communicate the potential of the technique
- share best practice on how to communicate with water authorities on these issues
- promote the use of this methodology across Europe, via the member states and the regions

More information on the INPAR network can be found on the website (http://www.irmm.jrc.be/html/activities/isotopic_measurements/INPAR/).

6. INPAR cases studies

Few specific case studies across Europe are presented bellow:
The main issues addressed are:

- What is the issue, from the perspective of policy implementation, implementation of legislation, remediation ?
- What is the approach used in each specific case ? Kind of measurement data used ? Why can the above issue not be solved using non-isotope approach ?
- Brief explanation on the sampling strategy and the main conclusion of the case study
- Literature reference for each case study

6.1. Source apportionment of nitrate pollution in surface water using stable isotopes of N and O in nitrate and B isotopes

Authors: F. Accoe[1], M. Berglund[1], S. Duta[1], C. Hennessy[1], P, Taylor[1]
K.Van Hoof[2], S. De Smedt[2]

Institution: [1]Institute for Reference Materials and Measurements, Joint Research Center-European Commission, B-2440, Geel, Belgium
[2] Flamish Environment Agency, B-9320, Erembodegem, Belgium

Collaboration with other institutions, environmental agency or stakeholders
Gent University, Laboratory of Applied Physical Chemistry - ISOFYS, Belgium

6.1.1 What is the issue, from the perspective of policy implementation, implementation of legislation, remediation

The issue in general: in agricultural areas in Flanders, excess application to fields of animal manure and mineral N fertilizers is generally assumed to be the major source of nitrate pollution in surface water. Despite extensive policy measures taken to reduce nitrate input from agricultural sources (three consecutive Manure Action Plans or MAPs have been initiated since 1996), improvement in surface water quality is stagnating during the last 5 years (Fig. 2) and elevated nitrate concentrations (>50 mg NO^{-3} L^{-1}) are currently still observed in 42% of the MAP surface water monitoring points

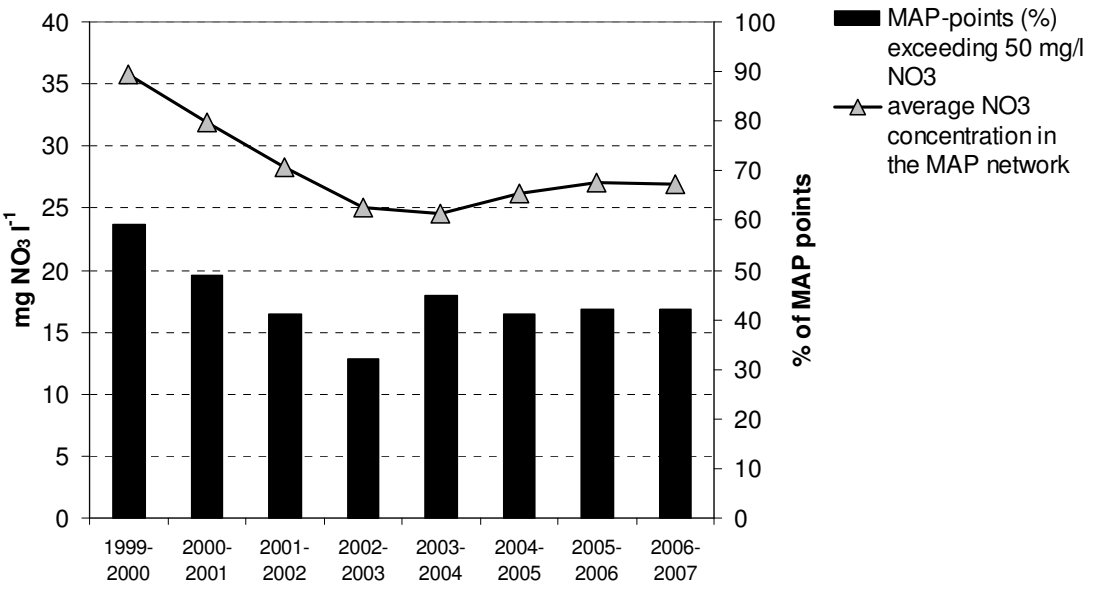

Fig. 2. Evolution of the average nitrate concentration since 1999 in the MAP surface water monitoring network in Flanders and percentage of the MAP points with nitrate concentrations exceeding 50 mg NO^{-3} L^{-1} at least once per year (data from Flemish Environment Agency).

The Flemish Environment Agency (VMM) *suspects* (but could not prove) that in some of these areas domestic sewage or discharges containing mineral fertilizers from hydroculture in greenhouses are also contributing. Thus appropriate remedial measures could not be implemented (connecting houses to the public sewage system, legislation controlling discharges from hydroculture).

The specific issue: In this case, VMM suspects nitrate input from discharges of domestic sewage into the surface water in a region where houses are not yet connected to the public sewer system. There is

an ongoing discussion between local environmental managers and the agricultural sector about the significance of these discharges relative to the input from animal manure in this region.

What is the approach used in this specific case. Kind of measurement data used. Why can the above issue not be solved using non-isotope approach

The general approach used so far (in both cases) was monthly monitoring by VMM of the concentrations of ions (nitrate, nitrite, chloride, ammonium, orthophosphate) and dissolved oxygen, pH and electrical conductivity in a surface water sampling network (MAP points).
The long term evolution of the nitrate concentrations monitored in a MAP point in this region is shown in Fig. 3. Most elevated nitrate concentrations are usually observed here during winter period, when nitrates are more easily transported to surface water due to reduced plant uptake and soil coverage and more intense rainfall.
Evolution of the nitrate concentration is affected by nitrate inputs but also by environmental conditions (rainfall, temperature) and natural nitrate removal processes (denitrification). Therefore, interpretation of the monitored nitrate concentrations to evaluate remedial measures taken is complicated and does not enable to identify the sources of nitrate pollution (manure or domestic sewage).

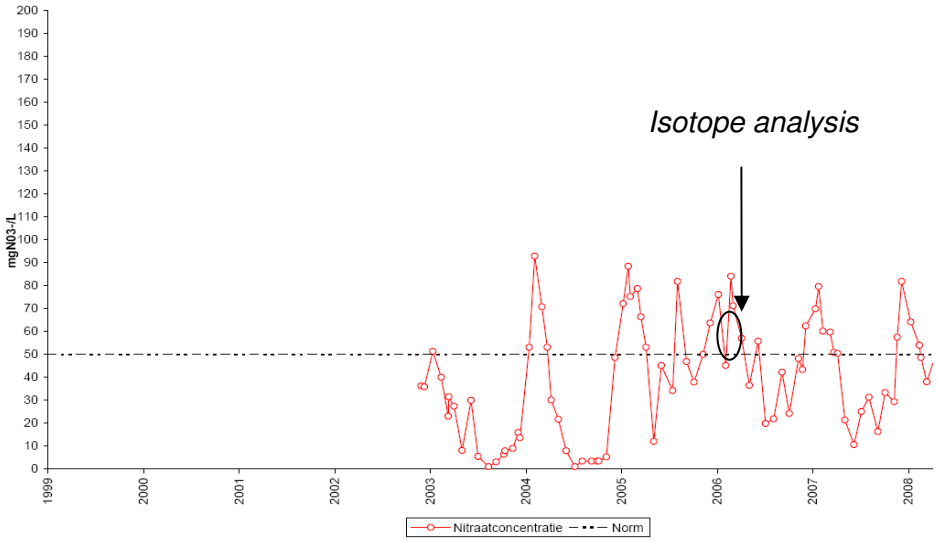

Fig. 3. Long term evolution of the nitrate concentration monitored in a MAP point where input from domestic sewage is suspected

Briefly explain the sampling strategy and the main conclusions of the study

The sampling strategy:

- A surface water sample for isotope analysis was taken by VMM in April 2006 from 3 MAP points in the study area (Fig. 2), situated in the northern region of Flanders (Belgium, part of the Meuse river basin)
- Samples from the potential nitrate sources in the study area (manure, domestic sewage, mineral N fertilizers, soil N, atmospheric deposition) were also collected for isotope analysis.
- N and O isotope analysis ($\delta^{15}N$ and $\delta^{18}O$ values) and B isotope analysis ($\delta^{11}B$ value) were executed on the water samples and nitrate source samples.

How did the isotope approach help to understand/solve the issue. Were counterintuitive conclusions obtained. Did the isotope approach support the implementation of more effective remedial actions or legislation

Nitrate N ($\delta^{15}N$) combined with B isotope values ($\delta^{11}B$) (Fig. 4) showed that nitrate pollution at this location could be largely attributed to excess manure application and that there was no significant input from domestic sewage.

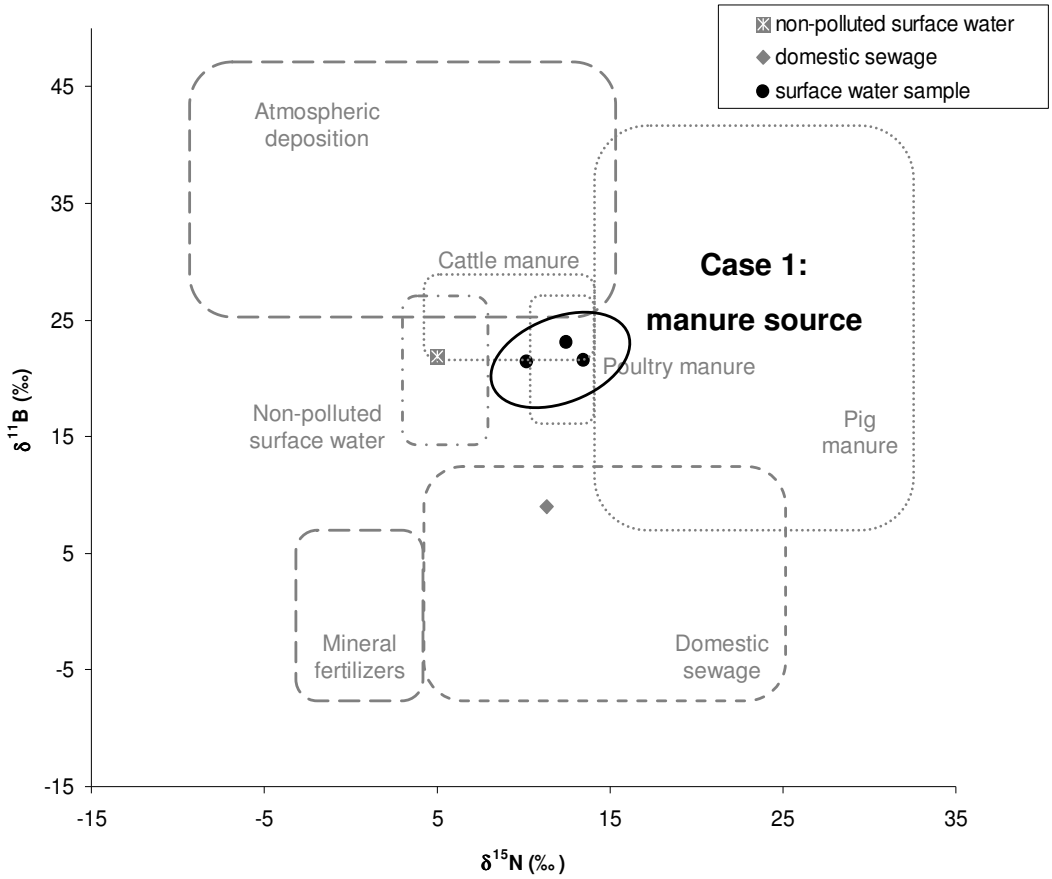

Fig. 4. Nitrate nitrogen ($\delta^{15}N$) versus boron isotope values ($\delta^{11}B$) in nitrate source samples and surface water samples

The isotope approach help to understand/solve the issue as following:

- Isotope data showed that there was no significant contribution from domestic sewage in sampling points where this was suspected by VMM.
- Efforts to connect houses to the public sewer system would thus not be effective in this region to reduce nitrate pollution.

Reference

- F. Accoe, M. Berglund, S. Duta, C. Hennessy, P. Taylor: Source apportionment of nitrate pollution in surface water using stable isotopes of N and O in nitrate and B isotopes: a case study in Flanders, Belgium, EUR 23425 EN, 2008, ISBN 978-92-79-094-60-6

The second case in the frame of same study on the source apportionment of nitrate pollution in surface water using stable isotopes of N and O in nitrate and B isotopes is also presented below.

6.1.2 What is the issue, from the perspective of policy implementation, implementation of legislation, remediation

The special issue: In this case, VMM suspects nitrate input from discharges containing mineral fertilizers originating from hydroculture in a region with intensive greenhouse cropping.

What is the approach used in this specific case. Kind of measurement data used. Why can the above issue not be solved using non-isotope approach

The approach used so far was monthly monitoring by VMM of the concentrations of ions (nitrate, nitrite, chloride, ammonium, orthophosphate) and dissolved oxygen, pH and electrical conductivity in a surface water sampling network (MAP points).
The long term evolution of the nitrate concentrations monitored in a MAP point in this region is shown in Fig. 5. Elevated nitrate concentrations are observed here during the entire year. This can not be explained by manure inputs alone, which indicates the presence of other nitrate sources.

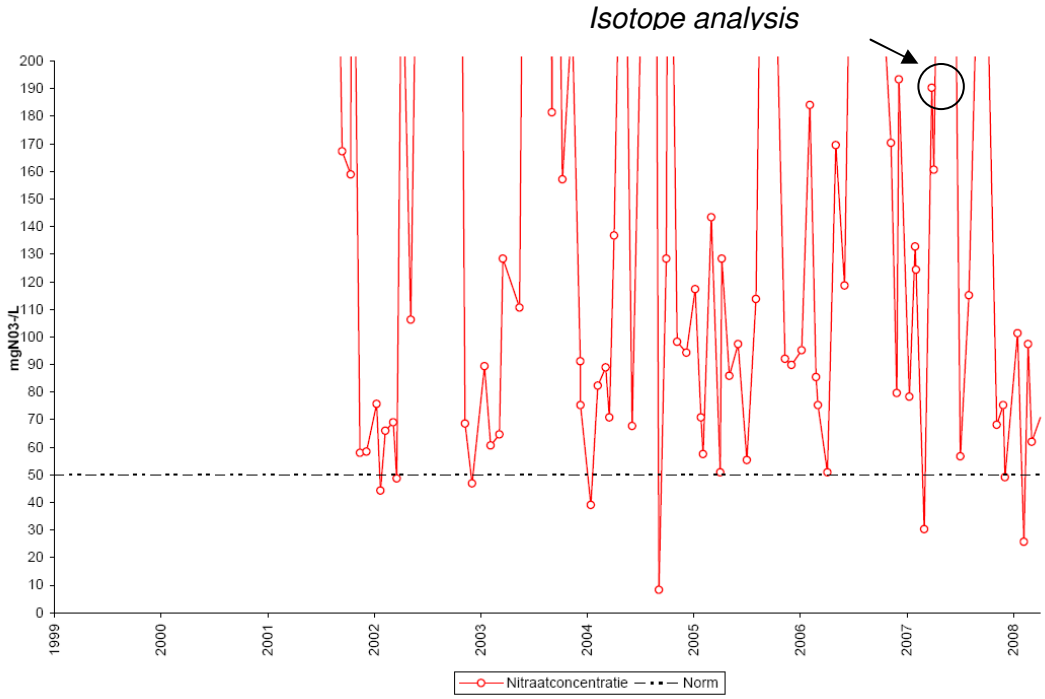

Fig. 5. Long term evolution of the nitrate concentration monitored in a MAP

Briefly explain the sampling strategy and the main conclusions of the study

The sampling strategy was:

- A surface water sample for isotope analysis was taken by VMM in April 2007 (Fig. 5) from 3 MAP points in the study area, situated in the central region of Flanders (part of the Nete river basin)
- Samples from the potential nitrate sources in the study area (manure, domestic sewage, hydroculture, mineral N fertilizers, soil N, atmospheric deposition) were also collected for isotope analysis.
- N and O isotope analysis ($\delta^{15}N$ and $\delta^{18}O$ values) were executed on the water samples and nitrate source samples.

Some conclusions:
The elevated $\delta^{18}O$ values indicate a significant input of mineral nitrate fertilizers potentially originating from hydroculture, in addition to nitrate from animal manure or sewage (Fig. 6).

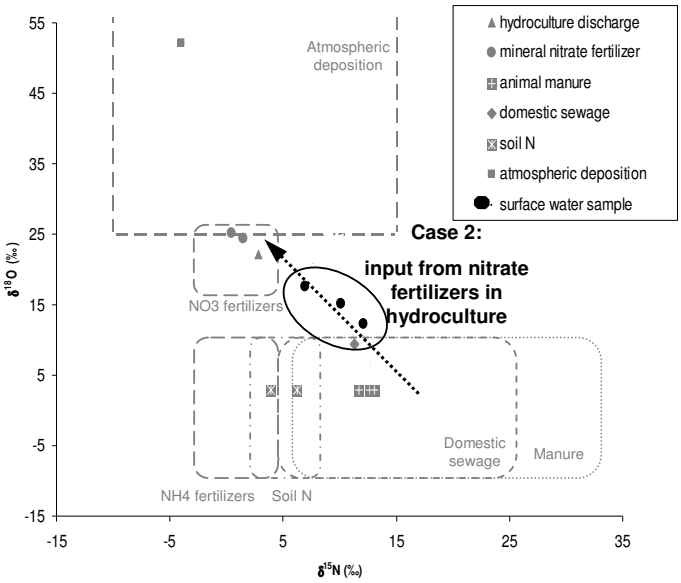

Fig. 6. Nitrate oxygen ($\delta^{18}O$) versus nitrogen isotope values ($\delta^{15}N$) in nitrate sources and surface water samples

How did the isotope approach help to understand/solve the issue. Were counterintuitive conclusions obtained. Did the isotope approach support the implementation of more effective remedial actions or legislation

The isotope approach help to understand/solve the issue as followig:

- Isotope data indicated that discharges from hydroculture activities potentially contribute to the nitrate pollution observed in this case.
- Implementation of measures to control discharges from hydroculture are thus needed, to reduce nitrate pollution originating from this source

Reference:

- F. Accoe, M. Berglund, S. Duta, C. Hennessy, P. Taylor: Source apportionment of nitrate pollution in surface water using stable isotopes of N and O in nitrate and B isotopes: a case study in Flanders, Belgium, EUR 23425 EN, 2008, ISBN 978-92-79-094-60-6

6.2. A regional survey on nitrate contamination of the Po valley alluvial aquifer (Northern Italy)

Authors: E. Sacchi[1], G. Pilla[2], L. Gerbert-Gaillard[3], G.M. Zuppi[4]

Institution: [1] Dipartimento di Scienze della Terra, Università di Pavia and CNR-IGG, Sezione di Pavia, Italy
[2] Dipartimento di Scienze della Terra, Università di Pavia, Italy
[3] ISO4 s.s., Pavia, Italy
[4] Dipartimento di Scienze Ambientali, Università Ca' Foscari di Venezia, Italy

Collaboration with other institutions, environmental agency or stakeholders:

This study was supported by the Fondazione CRT (bank foundation) and by the provincial agencies for groundwater management and protection (Amministrazione Provinciale di Pavia, Amministrazione Provinciale di Alessandria, Amministrazione Provinciale di Novara). The work was conducted in close collaboration with the regional environmental monitoring agency (ARPA Piemonte, Dipartimenti di Alessandria e Novara).

What is the issue, from the perspective of policy implementation, implementation of legislation, remediation

The issue: The Po plain, located in Northern Italy, supports most of the agricultural and industrial activities of Northern Italy, which are associated with groundwater exploitation and pollution mainly in the shallower aquifers.
The Italian legislation on groundwater quality closely follows the European guidelines. Nevertheless both at national and regional level, the policy implementation has failed, especially concerning the " nitrate directive", having to face the strong opposition of several corporations, especially farmers. This has recently led to an infraction proceeding initiated by the EC.
At the local scale, the Piemonte region designated in 10/2002 the areas vulnerable to nitrate pollution, where the use of fertilisers, especially manure, was restricted, causing farmers to protest against the regulation. The Alessandria provincial administration questioned the extension of the vulnerable areas over its territory and wanted to prove that manure spreading was not generally the cause of high nitrate contents in groundwater.

What is the approach used in this specific case. Kind of measurement data used. Why can the above issue not be solved using non-isotope approach

The approach: A preliminary selection of samples for hydrochemical and isotopic characterisation was performed based on available data from groundwater quality monitoring programmes. About 100 monitored wells and natural outflows were selected, considering also rivers and irrigation channels, all with nitrate concentration exceeding 50 mg/l.
Samples were analysed for their major ion concentration (especially nitrate, sulphate and chloride content), and stable isotopes of the nitrate molecule. In specific cases, trace metals, stable isotopes of the water molecule and $\delta^{13}C$ were also used**.**
Agricultural regions commonly suffer diffuse water pollution, which cannot be attributed to a precise source, resulting from the cumulative effect of day to day activities over large areas, including application of synthetic fertilisers, manure spreading and sewage sludge disposal. The designation of vulnerable areas is made based on groundwater nitrate content, which is measured in some wells and extrapolated to the surrounding areas with common interpolation software, regardless of the quality of the original data.

Briefly explain the sampling strategy and the main conclusions of the study

The sampling strategy: The study investigates the origin, distribution and fate of dissolved nitrates in groundwater from the shallow Po plain alluvial aquifer, of Quaternary age, constituted by gravels and sands with interbedded clay layers. The area covered by this study is of approximately 3,600 km^2, crossing the Po plain from N to S in correspondence to the Piedmont-Lombardy administrative boundary. Agricultural land use includes corn, wheat and rice fields.

A preliminary selection of samples for hydrochemical and isotopic characterisation was performed based on available data from groundwater quality monitoring programmes. About 100 monitored wells and natural outflows were selected, considering also rivers and irrigation channels, all with nitrate concentration exceeding 50 mg/l.

How did the isotope approach help to understand/solve the issue. Were counterintuitive conclusions obtained. Did the isotope approach support the implementation of more effective remedial actions or legislation

Results indicate that the type and distribution of groundwater contamination is closely related to:

1. the hydraulic characteristics of the unsaturated zone: clay rich soils reduce infiltration and favour denitrification through the establishment of anoxic conditions

2. the agricultural input: corn and wheat cultivation seems to be mostly responsible for nitrate contribution to groundwater (large use of synthetic fertilisers)

3. irrigation practices: the artificial recharge associated with rice cultivation also represents a preferential pathway for input of exotic substances to groundwater, but in this case, the input of nitrogen compounds is partially reduced by denitrification.

The isotopic composition of nitrates also indicates that, in the Po plain, the depth of the denitrification zone is strongly conditioned by the presence of buried structures and associated saline waters: it may be as shallow as 15 m below surface, like in the Oltrepo region, or deeper than 100 m, like in the Alessandria plain. Therefore stable isotopes of the nitrate molecule may also represent a useful tool to evidence aquifer overexploitation associated with high withdrawal rates.

Some conclusions: This study dramatically evidences the impact of intense agriculture activities over groundwater resources. Contamination from synthetic fertilisers is widespread and nitrate accumulation is a threat to large groundwater supplies. Peak concentrations are instead associated to point source pollution and can be attributed to leakage of the sewage network. Very little non-point source contamination seems to originate from manure spreading.

The results of the study have been presented at the provincial and regional level, but with little positive feedback. The main objection was that the regulators need to discriminate in an unambiguous way between manure contamination and leaking sewage network, which cannot be achieved only by the use of nitrogen isotopes. Only recently, the Lombardy region has launched a 3 years project with the objective of tracing sources, pathways and fate of nitrates, including also the use of boron strontium and nitrate isotopes.

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- Sacchi E., Pilla G., Gerbert-Gaillard L., Zuppi G.M. (2007) - A regional survey on nitrate contamination of the Po valley alluvial aquifer (Northern Italy). Int. Symp. on Advances in Isotope Hydrology and its role in Sustainable Water Resources Management, IAEA, Vienna 21-25 May 2007, IAEA-CN-151/34, vol., 2, 471-478

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6.3. Combination of $\delta^{15}N$ and $\delta^{18}O$ values of nitrate to identify nitrate sources in surface water in Flanders, Belgium

Authors: D. Xue[1], P. Boeckx[1], B. De Baets[2], J. Botte[1], and Kor Van Hoof[3]

Institution: [1]Laboratory of Applied Physical Chemistry - ISOFYS, Gent University Belgium
[2] Research Unit Knowledge-based Systems, Gent University, Belgium
[3] Flemish Environmental Agency, Belgium

Collaboration with other institutions, environmental agency or stakeholders
Institute for Reference Materials and Measurements, Joint Research Center, European Commission

What is the issue, from the perspective of policy implementation, implementation of legislation, remediation
The vast amount of reactive nitrogen present in surface waters in Flanders (Belgium) is an environmental problem. This is caused by intensive agricultural land use, increased use of fertilizers and manure, and discharge of human sewage. The implementation of the Nitrate Directive (EC, 2002) in Europe established a detailed framework for the protection of waters due to nitrate pollution from agricultural sources. While this directive imposed maximum allowable nitrate concentrations (50 NO_3^- [1] mg L^{-1}) and initialized an extensive nitrate monitoring campaign, some regions continue to show elevated if not increasing nitrate levels (VMM, 2005). Nitrate concentration data alone can not fully assess the source and extent of surface water nitrate inputs, which are key aspects of effective management strategies. Therefore a research project is conducted to develop and evaluate a mathematical classification model to identify nitrate sources in surface water in Flanders, on the basis of existing physical-chemical surface water data (T, pH, EC20, NH_4^+, NO_2^-, NO_3^-, Cl^-, O_2, O_{2sat}, PO_4^{3-}) from 2003 to 2008 and stable isotope ratios of nitrate.

What is the approach used in this specific case. Kind of measurement data used. Why can the above issue not be solved using non-isotope approach

The approach: A preliminary decision tree model was built based on historical physico-chemical data of 47 sample points, in which missing data were replaced via "singular spectrum analysis" and Fourier transform has been applied as an effective data-preprocessing method to obtain good quality data for building a decision tree model. The optimum correct classification result we can get is 94% for the available dataset after Fourier transformation. The correctly classified percentages for five nitrate classes are: 91% for class A, 94% for class B, 97% for class C, 98% for class D and 85% for class E. There was a relatively low correct classification result in class E, which required further (isotopic) investigation.
It has been accepted that the $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 values of nitrate can provide useful information on the sources of nitrate in water, as different nitrate sources (fertilizer, manure, industrial/septic waste, and atmospheric N deposition) have unique isotopic ratios of nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$). To further improve nitrate sources classification, 30 sample sites (5 classes x 6 sample points per class) of the 47 above mentioned sample points were selected for isotopic ($\delta^{15}N$- and $\delta^{18}O$-NO_3^-) and physico-chemical monitoring (T, pH, EC20, NH_4^+, NO_2^-, NO_3^-, Cl^-, O_2, O_{2sat}, oPO_4^{3-}) from October 2007 to September 2009. The sampling frequency is once per month for each sample point.

Briefly explain the sampling strategy and the main conclusions of the study

The sampling strategy: VMM (Flemish Environmental Agency) manages an operational network, monitoring about 800 sample points for surface water quality. VMM has provided 47 sample points which are distributed over entire Flanders and allocated by VMM and Boerenbond (Farmers

organization) into five classes with different nitrate sources: class A contains 11 sample points and greenhouses are considered as the nitrate source; class B has 7 sample points and agriculture is considered as the main nitrate source; class C has 15 sample points and the nitrate source is considered as agriculture with ground water compensation; class D has 8 sample points and the nitrate source is considered as households; and class E belonging to a combination of horticulture and agriculture, has 6 sample points.

How did the isotope approach help to understand/solve the issue. Were counterintuitive conclusions obtained. Did the isotope approach support the implementation of more effective remedial actions or legislation

Some conclusions: The analytical techniques to determine $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ are "anion exchange method" (Silva et al., 2000) and "bacterial denitrification method" (Sigman et al., 2001). Three sample points from the 30 have been selected to perform a comparison of both techniques. So far, we observed that there is typical 1-2‰ variation in N and O isotopic results between the two techniques. The "bacterial denitrification method" is used to determine the $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ for the 30 sample points. Preliminary 3-month average values of $\delta^{15}N$- and $\delta^{18}O\text{-}NO_3^-$ for 30 sample points are displayed in Fig. 1, and those isotopic values range from 4.9 to 28.0‰ for $\delta^{15}N$ and -1.3 to 22.7‰ for $\delta^{18}O$ (Fig. 7).
These preliminary data indicate that nitrate sources are dominated by manure or sewage. If we plot the average value of isotopic ratios for each class (from class A to class E), we can see all five nitrate classes are dominated by manure or sewage as nitrate source (Fig. 8). However, denitrification and mixture of nitrate sources may give rise to uncertainties of nitrate source identification. Hence, we need a multiple isotopic approach ($\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$ and $\delta^{11}B$) for nitrate source identification and analyses of original N source material, which will be collected on those farms surrounding the 30 sample points.

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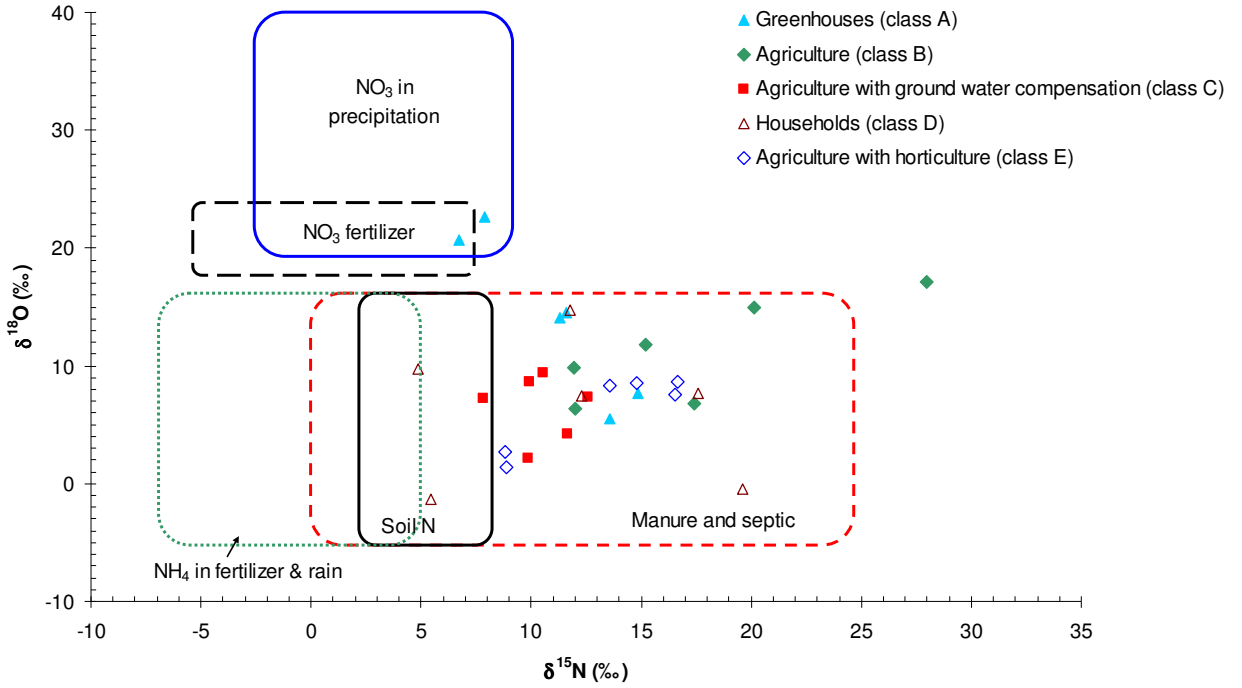

Fig.7 Preliminary 3-month average values of δ^{15}N- and δ^{18}O-NO_3^- for 30 sample points.

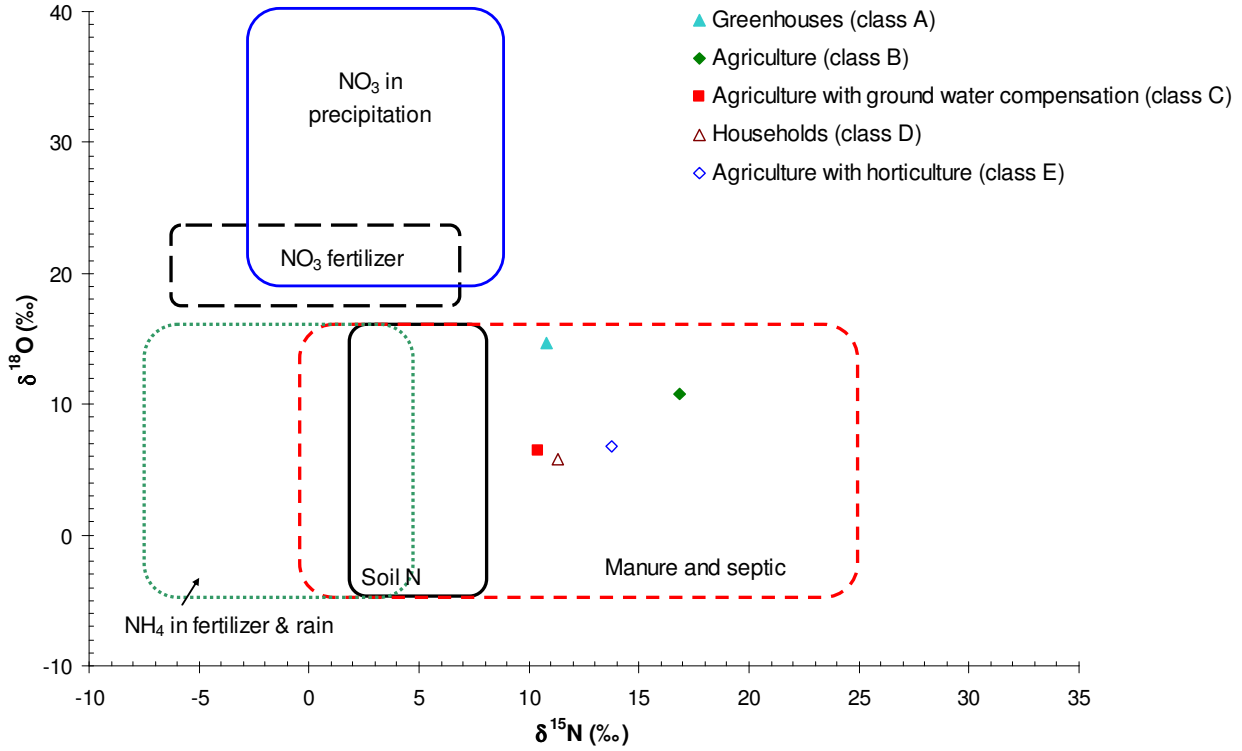

Fig. 8. Preliminary 3-month average of δ^{15}N- and δ^{18}O-NO_3^- for five nitrate classes.

6.4. Environmental isotopes (N, S, C, O, D) to determine natural attenuation processes in nitrate contaminated waters: example of Osona (NE Spain)

Authors: L. Vitòria, A. Soler, À. Canals and N. Otero

Institution: Grup de Mineralogia Aplicada i Medi Ambient, Departament de Cristalografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Spain
Departament de Geologia Ambiental, Institut de Ciències de la Terra "Jaume Almera", CSIC

Collaboration with other institutions, environmental agency or stakeholders
Agència Catalana de l'Aigua (Water Agency of the Catalonian Government)

What is the issue, from the perspective of policy implementation, implementation of legislation, remediation

The aim of this study was to integrate chemical and stable isotope data of groundwater in the Osona region (NE Spain) in order to evaluate the state of the water resources and predict their evolution. In the area, pig manure had been intensively used as organic fertilizer producing diffuse nitrate contamination, although synthetic fertilizers were also occasionally used. Therefore, the multi-isotopic approach (^{15}N, ^{34}S, ^{13}C, ^{18}O, D) coupled with the chemical data, was applied first to validate their use as tracers of nitrate sources, and, secondly as markers of nitrogen processes. In particular, the nitrification process was evaluated using the $\delta^{18}O_{NO3}$ value; the amount of denitrification was estimated taking into consideration both the chemical and the $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ data. Furthermore, the denitrification reactions were determined to some extent applying a multi-isotopic approach ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$). This knowledge is important when designing water and agricultural control and management plans.

What is the approach used in this specific case. Kind of measurement data used. Why can the above issue not be solved using non-isotope approach

A multi-isotopic approach was used to characterize an area polluted with nitrate form organic manure. This study was designed to compare the isotopic signature of nitrate in swine manure with the isotopic composition of groundwater polluted with manure, as the isotopic signature of nitrate in groundwater could differ from the original source, as nitrogen could be affected by several processes as volatilization, nitrification and denitrification. Furthermore, denitrification processes (a natural attenuation of nitrate pollution) were evaluated by means of the isotopic composition. The evaluation of the degree of denitrification is very difficult to obtain using chemical data alone, especially in an area with no adequate infrastructure. The study was also considered as a point of departure, the results obtained should allow applying the isotopic tools to "mixed areas" where both chemical and organic fertilizers are applied.

Briefly explain the sampling strategy and the main conclusions of the study

Thirty eight groundwater samples were collected during October 2001. The chemical characterization included major ions (Cl^-, $SO_4^=$, HCO_3^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}), TOC and NH_4^+. The isotopic characterisation comprised the stable isotopes of water (δD and $\delta^{18}O$), and the isotopic composition of dissolved nitrate ($\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$), dissolved sulphate ($\delta^{34}S_{SO4}$, and $\delta^{18}O_{SO4}$), and dissolved inorganic carbon ($\delta^{13}C_{DIC}$).

The coupled use of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ confirmed the link between groundwater nitrate pollution and pig manure. While most samples had isotopic values in the range of pig manure nitrate, one sample

had a clear signature of synthetic fertilisers and four showed intermediate values, suggesting a mix between these two sources (Fig. 9). Nitrate isotopic data suggested that denitrification processes were taking place. Moreover, the occurrence of this process was confirmed using $\delta^{18}O_{NO3}$ coupled with the NO_3^-/Cl^- ratio, thus avoiding the influence of continuous nitrate inputs. A further insight into denitrification processes was obtained using a multi-isotopic approach, analyzing the ions involved in denitrification reactions ($\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{18}O_{H2O}$ and $\delta^{13}C_{DIC}$).

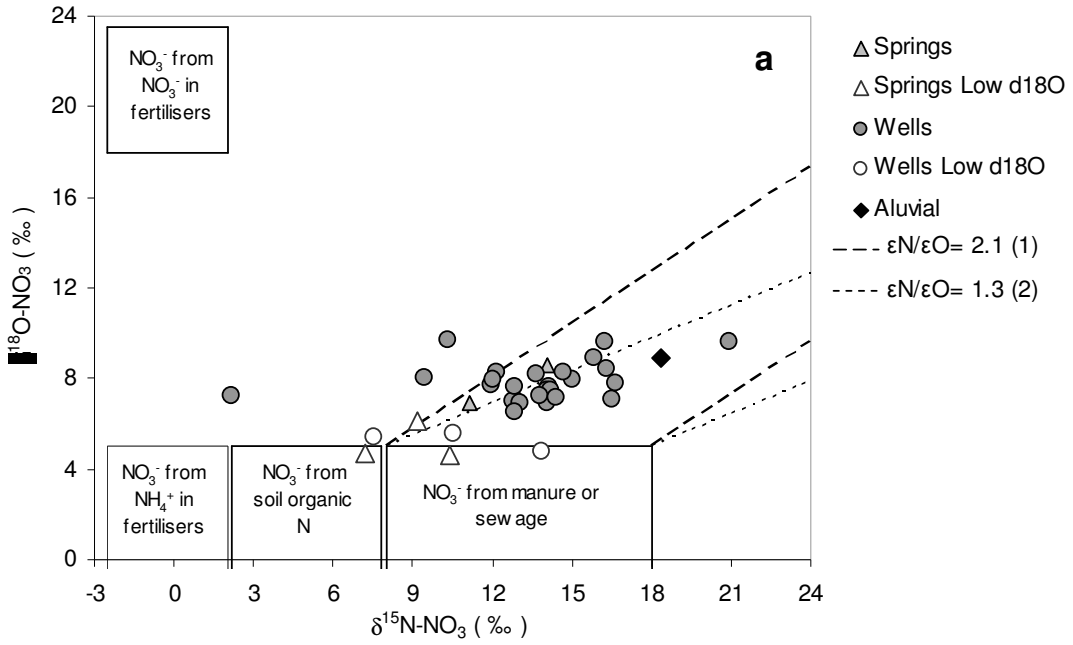

Fig. 9. $\delta^{15}N$ vs. $\delta^{18}O_{NO3}$ diagram. Boxes represent the isotopic composition of NO_3^- from different sources (Mengis et al. 2001); lines represent the changes in the isotopic composition due to denitrification processes. The different slopes represent the extreme values from the literature for εN/εO (1) Bottcher et al. (1995), (2) Fukada et al. (2003).

This approach showed a link between denitrification and pyrite oxidation; however, the role of organic matter oxidation could not be confirmed nor discarded with the available information. In areas, such the studied one, where aquifers are complex, and with no good infrastructure (e.g. multi-piezometers) to describe groundwater dynamics, isotopes provide effective tools to trace sources of contamination and study processes affecting nitrogen.

How did the isotope approach help to understand/solve the issue. Were counterintuitive conclusions obtained. Did the isotope approach support the implementation of more effective remedial actions or legislation

The isotope approach permitted to identify the source of nitrogen in an area where, although the main fertilization had an organic origin, also chemical fertilizers were applied. The coupled use of nitrogen and oxygen isotopes allowed to distinguish some samples with nitrate from chemical fertilizers, or with a mixed signature, from those polluted with organic manure. In a parallel work, conducted in an area where the main nitrogen source is related to chemical fertilizers (see the first case study in the Maresme area), results showed that these two sources chemical fertilizers and organic manure could be distinguished analyzing nitrogen and oxygen isotopic composition of dissolved nitrate. In addition, denitrification processes were identified and the degree of denitrification was calculated to some extent. The application of a multi-isotopic approach allowed to determine which reactions control the natural attenuation of nitrate, a useful information to asses the future evolution of nitrate pollution.

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6.5. Environmental isotopes (N, S, C, O, D) to determine natural attenuation

Authors: L. Vitòria, A. Soler, R. Aravena and À. Canals

Institution: Grup de Mineralogia Aplicada i Medi Ambient, Departament de Cristalografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Spain and Earth Environmental Sciences Department, Faculty of Science, University of Waterloo, Canada.

Collaboration with other institutions, environmental agency or stakeholders
Agència Catalana de l'Aigua (Water Agency of the Catalonian Government)

What is the issue, from the perspective of policy implementation, implementation of legislation, remediation

The aim of this study was to characterise chemical and isotopic nitrate contaminated groundwater in an area polluted by the use of synthetic fertilisers due to a very intensive agricultural activity. This study was carried out in the Maresme region situated close to the Mediterranean Sea shoreline. For more than 50 years, groundwater in this region has been intensively exploited for agricultural purposes, causing an alteration of the aquifer hydrodynamics and therefore a progressive seawater intrusion. This study was part of a research project aiming to apply the isotope approach to study the origin of nitrate in contaminated groundwater throughout Spain. The approach included the isotope characterisation of nitrate in contaminated sites with well-known nitrate sources in order to elucidate the nitrate contribution in other polluted areas where nitrate comes from different sources.

What is the approach used in this specific case. Kind of measurement data used. Why can the above issue not be solved using non-isotope approach

A multi-isotopic approach was used to characterize an area polluted with nitrate form chemical fertilizers. This study was designed to compare the isotopic signature of nitrate in chemical fertilizers with the isotopic composition of groundwater polluted with chemical fertilizers, as the isotopic signature of nitrate in groundwater could differ from the original source, as nitrogen could be affected by several processes as volatilization, nitrification and denitrification. The study was also considered as a point of departure, the results obtained should allow applying the isotopic tools to "mixed areas" where both chemical and organic fertilizers are applied.

Briefly explain the sampling strategy and the main conclusions of the study

Eight groundwater samples were collected during October 2000, also eleven of the most frequently used fertilisers in the region were also analysed. The chemical characterization included major ions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}), TOC and NH_4^+. The isotopic characterisation comprised the stable isotopes of water (δD and $\delta^{18}O$), and the isotopic composition of dissolved nitrate ($\delta 1^{15}N_{NO3}$, $\delta^{18}O_{NO3}$), and dissolved sulphate ($\delta^{34}S_{SO4}$, and $\delta^{18}O_{SO4}$).

Chemical and isotope data of these waters were used to identify and evaluate the nitrate contamination, as well as the sources of sulphate and chloride in the area. The enriched $\delta^{15}N_{NO3}$ values (+6.8‰ and +9.4‰) obtained in the groundwater compared to the $\delta^{15}NN_{total}$ values of fertilisers (–1.1‰ and +3.9‰) indicated the occurrence of ammonia volatilisation and nitrification reactions in the study site. The $\delta^{18}O_{NO3}$ values in groundwater, ranging between +5.1‰ and +10.2‰, did not showed a significant contribution of the fertilisers enriched $\delta^{18}O_{NO3}$ signatures (+21.8‰ and +24.8‰, with one value of +48.5‰), except for two samples that seemed to have a larger influence of nitrogenous fertilisers (Fig.10). The ^{18}O pattern suggested that the fertilisers nitrate component is recycled in the unsaturated

zone. Denitrification reactions were not occurring in the studied area due to water re-circulation in an oxidising environment that did not permit this process to take place.
The $\delta^{34}S_{SO4}$ of groundwater (from +5.8 to +7.0‰) discarded a significant contribution of seawater (+20.3‰) as a sulphate source. Also, δD and $\delta^{18}O$ in groundwater did not show a significant influence of the marine isotopic signature. Therefore, the high chloride concentrations found in groundwater could be associated to salt accumulation from the intensive use of fertilisers, thus questioning the role of seawater intrusion as a source of chloride in the area.

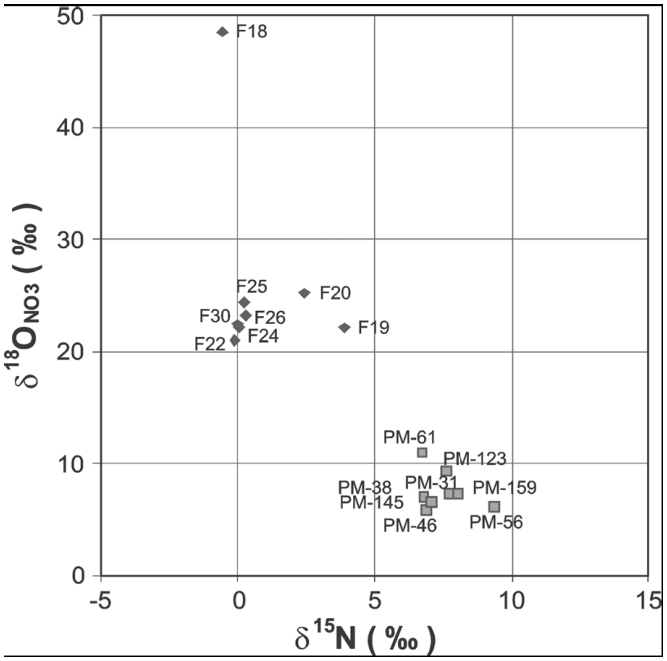

Fig. 10. $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$ and $\delta^{15}N_{Ntotal}$ from groundwater samples and fertilisers, respectively (PM: groundwater, F: fertilizer).

How did the isotope approach help to understand/solve the issue. Were counterintuitive conclusions obtained. Did the isotope approach support the implementation of more effective remedial actions or legislation.

The isotope approach permitted to identify the occurrence of volatilization and nitrification processes, and allowed to determine the resulting isotopic composition in groundwater polluted with chemical fertilizers. In a parallel work, conducted in an area where the main nitrogen source is of organic origin (see the second case study in the Osona area), results showed that these two sources chemical fertilizers and organic manure could be distinguished analyzing nitrogen and oxygen isotopic composition of dissolved nitrate. In addition, using the isotopic composition of water and dissolved sulphates, allowed to link the high chloride contents in the intensive use of fertilizers, and discard a major contribution of seawater intrusion.

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6.6. Chemical, isotopic and microbiological evidence for nitrification below the plant root zone from intensive fertilized agricultural areas in Austria - Insights from lysimeter studies and soil cores

Authors: A. Leis

Institution: JOANNEUM RESEARCH Forschungsgesellschaft mbH, Institute of Water Resources Management (WRM), Hydrogeology and Geophysics

Collaboration with other institutions, environmental agency or stakeholders
Government of Styria, co-financed by EU/ERDF

What is the issue, from the perspective of policy implementation, implementation of legislation, remediation
The intensive use of organic and inorganic fertilizers has led to increased loads of nitrate in groundwater in many regions of Europe. The Leibnitzer Field aquifer of Styria in southern Austria has seen a strong increase in groundwater nitrate concentrations over the past decades. This aquifer is extremely susceptible to surface derived contamination because of its largely unconfined nature and highly permeable sands and gravels. The source of nitrate contamination in the aquifer is attributed to local, long term agricultural land use practices such as spreading large amounts of liquid manure (mainly from pigs) above the soils. To determine what action should be taken to reduce nitrate contamination of groundwater, it is important to identify the sources and the fate of nitrate in unsaturated zone, as well as the relevant microbiological processes. Compared to surface soils, relatively little is known about nitrogen transformation processes below the plant root zone. Therefore the objective of the study was to evaluate the main nitrogen transformation processes within and below the plant root zone using standard biogeochemical, isotopic and microbiological methods.

What is the approach used in this specific case. Kind of measurement data used. Why can the above issue not be solved using non-isotope approach
To investigate the occurrence and rate of nitrification in this zone a combination of chemical, microbial and isotopic techniques are used. We have used $\delta^{15}N$ and $\delta^{18}O$ isotope ratios of nitrate in unsaturated zone water samples obtained from the lysimeters in order to verify the results of the chemical and microbiological investigations with an independent method. In addition, selected samples also were analyzed for the carbon isotopic composition ($\delta^{13}C$-DIC) of dissolved inorganic carbon and the sulphur isotopic composition ($\delta^{34}S$) of sulphate-sulphur.
(10-15 lines)

Briefly explain the sampling strategy and the main conclusions of the study
The study has been conducted in the so called Leibnitzer Feld which is situated in the lower Mur valley in Styria (Austria) in the time from 1998 to 2001. Based on the knowledge that key processes which contributed to the nitrate problem in the Leibnitzer Feld predominantly take place in the unsaturated zone, an experimental lysimeter station was built in 1991. The station was designed to monitor the movement of water and solids from the atmosphere through the soil (~100 cm) and unsaturated sand and gravel (~450 cm) into the saturated quaternary valley fill. The station includes two non-weighable backfilled gravitation lysimeters (operating since 1991), six non-weighable monolithic field lysimeters (operating from 1991–2004), five seepage water samplers (operating from 1991–2004, two are still in operation) and various open field measurements. These included time-domain reflectometry (TDR) probes, gypsum blocks, tensiometers, and chemical sensors and suction cups and plates. The collected outflow of the suction plates and cups was analyzed over a number of years for hydrochemicals (major cations and anions, DOC) and isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$–DIC, $\delta^{15}N$–

NO_3 and $\delta^{18}O–NO_3$). In addition soil samples were taken from eight sampling points within the test field. The samples were collected every 30 cm from undisturbed soil profiles (0–240 cm). The soil samples collected for determination of the actual and potential nitrification activity, quantification of nitrifying bacteria and DNA-analyses (Fig. 11).

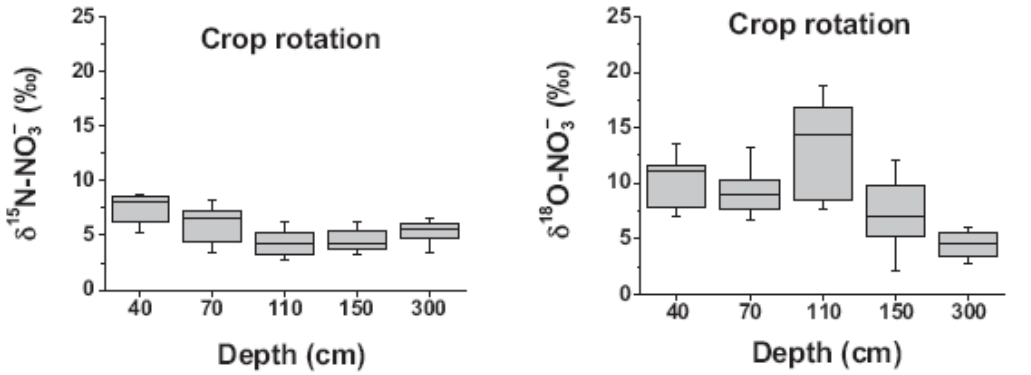

Fig. 8. Boxplot of $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ from lysimeters beneath crop rotation site for the period between May 1998 and April 1999.

Figure 11 and 12

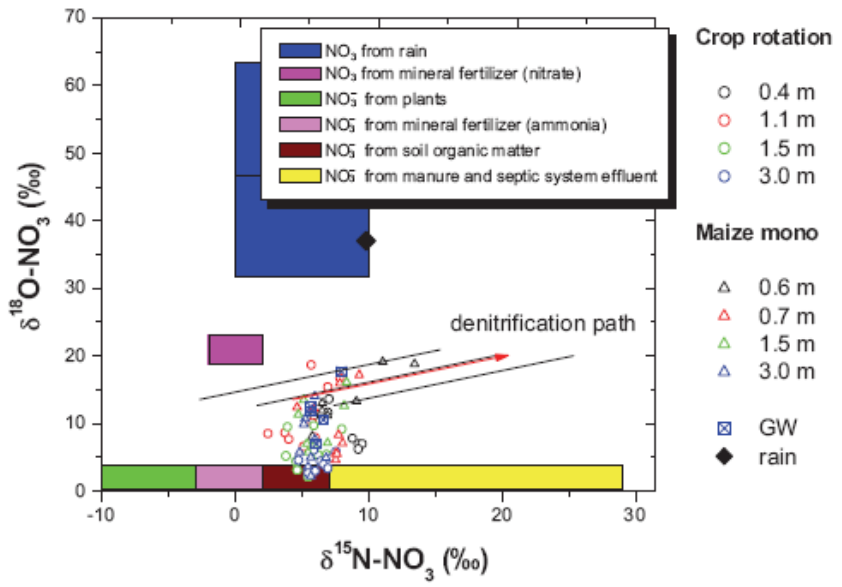

Fig. 9. Typical ranges for $\delta^{15}N$ and $\delta^{18}O$ values of nitrate from atmospheric deposition, nitrate containing mineral fertiliser and nitrification of ammonia derived from plant material, mineral fertiliser, soil organic matter, manure and septic system effluents. Also shown are the unsaturated zone water samples obtained from the lysimeters, groundwater and rain.

How did the isotope approach help to understand/solve the issue. Were counterintuitive conclusions obtained. Did the isotope approach support the implementation of more effective remedial actions or legislation

The isotopic composition of nitrate is not only a powerful tool to determining its sources, but can also provide information about nitrogen transformation processes such as nitrification and denitrification in the unsaturated zone. The combined use of $\delta^{15}N–NO_3$ – and $\delta^{18}O–NO_3$ – data confirmed that nitrate in the unsaturated zone was predominately derived from microbial nitrification and to a much lesser extent from atmospheric deposition (Fig. 12). The $\delta^{15}N–NO_3$ – and $\delta^{18}O–NO_3$ – data further suggested that nitrification can occur in the whole profile of the unsaturated zone. From this study it is concluded

that nitrification can occur below the plant root zone also and therefore plays a significant role in the speciation and transport of nitrogen compounds in the unsaturated zone.

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7. Conclusions

Many research activities are going on in different institutes across Europe using isotope techniques for management of nitrate pollution in water. Few of them, are summarised in this report as case studies. How such data can lead to source apportionment or detection of natural attenuation of nitrate pollution in surface and groundwater, how it is complementary to existing water quality monitoring data and how it enables those involved in the implementation of environmental policy to develop more effective remedial measures and management strategies are presented.

Using isotope techniques for management of nitrate pollution in water could be useful tool to solve some problems and to create awareness with environmental managers for the potential offered by the use of isotope data when tackling the environmental management of nitrate contamination in ground and surface water.

The INPAR network (Isotopes for improved management of Nitrate Pollution in Aqueous Resources) brings together the international expertise and stimulates the exchange of the multi-disciplinary know-how (stable isotope analysis, hydrogeology, (isotope) geochemistry, advanced statistical data analysis).

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Abstract

The objective of this report is to create awareness with environmental managers for the potential offered by the use of isotope data when tackling the environmental management of nitrate contamination in ground and surface water.
The report shows how such data can lead to source apportionment or detection of natural attenuation of nitrate pollution in surface and groundwater, how it is complementary to existing water quality monitoring data and how it enables those involved in the implementation of environmental policy to develop more effective remedial measures and management strategies.
The paper describes when and how to set up such studies, what can be expected as outcome and describes the benefits and limitations.
The above topics will be demonstrated via a number of case studies conducted in Europe where isotope data lead to a better understanding of the origin, degree of natural attenuation or transport processes of nitrate pollution in surface or groundwater.

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